Protective Oxidation of a Layer Structured Manganese Titanate, $Rb_xMn_xTi_{2-x}O_4$ (x = 0.75), in Acidic Solutions

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A layer structured manganese titanate $Rb_xMn_xTi_{2-x}O_4$ (x = 0.75) of the lepidocrocite type structure was oxidized with Ce^{4+} in sulfuric acid solutions. Although the titanate layer was dissolved into the acidic solutions without the oxidant, the layer showed high resistivity against the dissolution with the presence of Ce^{4+} ions, even in the same acidic conditions. A portion of the Rb ions were deintercalated corresponding to the amount of Mn^{3+} oxidized to Mn^{4+} in the manganese titanate layers.

Cation-exchangeable layer structured compounds can be useful host layers in the synthesis of interlayered pillar materials. The cations between the layers are ion-exchanged with positively charged precursors for oxide pillars such as hydroxy-metal cations like $[Al_{13}O_4(OH)_{24}]^{7+}$ and oxide sol particles;[1-4] upon calcination, the precursor cations are changed into oxide pillars, which keep the layers apart and form micropores between the layers corresponding to the dimensions and the population of pillars. Such layer structured compounds include layered silicates (clay minerals),[1-4] titanates,[5,6] and phosphates.[7] In a previous study,[8] we introduced silica pillars into a manganese titanate, $Rb_xMn_xTi_{2-x}O_4$ (x = 0.75), hereafter called $Rb_{0.75}MTO$. $Rb_{0.75}MTO$ has the lepidocrocite (γ-FeOOH) type layered structure;[9] Mn(III) and Ti(IV) occupy the Fe sites and O in the O and (OH) sites. Rb ions are located between the manganese titanate layers, balancing the negative charge formed by the replacement of Ti(IV) with Mn(III) (see Figure 1). The interlayer Rb cations were ion-exchanged with ammonium ions with long alkyl chains to open the interlayer space, followed by the hydrolysis of tetraethoxysilane (TEOS) between the layers. After burning off the organic parts, we successfully obtained silica pillared microporous titanates with a surface area as large as 500 to 850 m^2/g. Since the host titanate layer is a semiconductor, charge-transfer properties are expected for the resulting microporous structures.

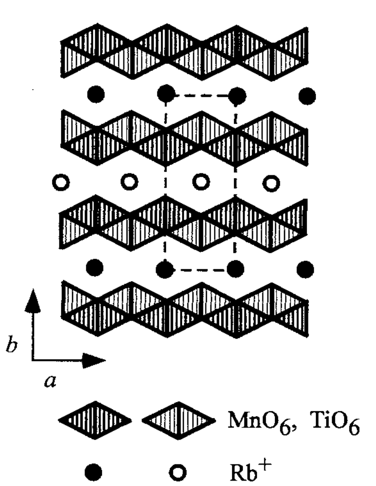

Figure 1. A schematic illustration of the structural model of $Rb_xMn_xTi_{2-x}O_4$ (x = 0.75). Mn and Ti ions are located at the octahedral sites.

The molecular sieving properties, or the microporous structures between the titanate layers must be affected by the cation exchange capacity, which will determine the amount of ammonium ions introduced between the layers, and in turn the amount of hydrolyzed TEOS as precursors of silica pillars between the layers. The direct synthesis of $Rb_xMn_xTi_{2-x}O_4$ with a reduced cation exchange capacity (x <0.6) by calcination did not give the layered compound, but a hollandite with a tunnel structure.[9] In this study, layer structured Rb_xMTO with a reduced charge capacity is prepared by the deintercalation of Rb ions from $Rb_{0.75}MTO$ via oxidation.

The preparation of $Rb_{0.75}MTO$ was described elsewhere.[9] It was oxidized in 0.5 M sulfuric acid solutions with varying amounts of $Ce(SO_4)_2$ under stirring for 15 h at room temperature. The added amount of Ce^{4+} was varied in the range of a molar ratio of $Ce/Rb_{0.75}MTO$ = 0 - 2 to obtain samples with different degrees of oxidation. After the reaction, the samples were separated by filtration with Teflon filters. The amounts of Rb, Mn and Ti dissolved into the solutions were measured on the filtrates using an inductively coupled plasma-atomic emission spectrometer (ICP-AES). The filtrates were also used to estimate the oxidation degrees of the solid products: the amount of Ce^{4+} in the filtrate was determined by back-titration with a Fe^{2+} solution using a ferroin indicator; the total concentration of Ce was determined by ICP-AES. Here, the oxidation degree shows how much % of the initial content of Mn^{3+} is oxidized to Mn^{4+}. The powder X-ray diffraction (XRD) patterns of the samples were measured using a Mac Science diffractometer (Model M18X-HF) with graphite monochromated Cu*K*α radiation.

The chemical analysis data of the oxidized $Rb_{0.75}MTO$ are summarized in Table 1. Note that about 30% of the manganese titanate layer was dissolved into the sulfuric acid solution when Ce^{4+} ions were not added. On the contrary, $Rb_{0.75}MTO$ showed high resistivity against the dissolution with the presence of Ce^{4+} ions even in the sulfuric acid solutions. The sample oxidized up to 58.4% was obtained with little dissolution of the titanate layer, and almost the corresponding amount of Rb ions (64.9% in $Rb_{0.75}MTO$) were deintercalated from the layer. It was found that the Ce ions were not taken up by the titanate layers. The difference between the amounts of oxidized Mn ions and deintercalated Rb ions can be attributed to H^+ ions taken up by ion-exchange.

Cation exchange properties of another lepidocrocite-type layered titanate, $Cs_x[Ti_{2-x/2}Mg_{x/2}]O_4$ (x = 0.7) was studied by

Table 1. Oxidation of $Rb_{0.75}MTO$ with Ce^{4+} in 0.5 M sulfuric acidic solutions

	Dissolution/ %			Oxidation/ %
$Ce^{4+}/Rb_{0.75}MTO$	Rb	Mn	Ti	
0	87.0	29.9	31.1	---
0.3	68.1	5.8	6.0	29.3
1.5	66.7	2.2	2.3	52.7
2.0	64.9	0.58	1.7	58.4

England *et al.*.[10] In that compound, Mg^{2+} ions replace the Ti^{4+} ions of the layers, and Cs^+ ions are located between the layers. They tried to prepare the hydrogen form by the exchange of Cs^+ with H^+ in HCl solutions. However, this layered titanate was rapidly dissolved into a 25% HCl solution at 60 °C, and a partial dissolution of about 40% was observed in a 10% HCl solution at 20 °C during stirring for 15 h. It was also reported that $LiMn_2O_4$ spinel was oxidized by the treatment with a HCl solution, where 1/4 of the manganese was brought into solution as Mn(II).[11] The end product was $Li_{0.04}MnO_2$ (λ-MnO_2). It appears that lower valent manganese ions and Mg^{2+} ions may not have resistivity against the attack by acid, and the binary titanate layers containing such metal ions are dissolved in acid. In the oxidation of $Rb_{0.75}MTO$ in sulfuric acids with the presence of Ce^{4+}, high valent Mn(IV) ions are formed on the surface of the particles. Mn(IV) sites will show resistivity against the attack by acid, and protect the titanate layers from the dissolution.

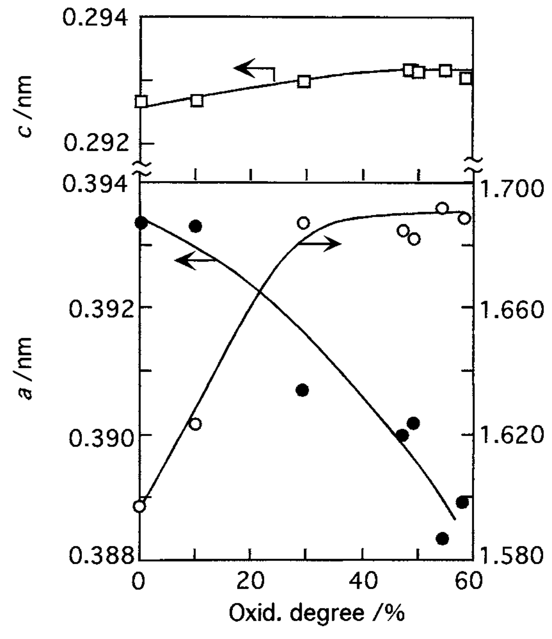

Figure 2. The lattice parameters of the oxidized samples as a function of the degree of oxidation.

The lattice constants of several oxidized samples prepared are shown in Figure 2 as a function of the degree of oxidation in %. The layer structure of the titanate was retained by the oxidation, and the lattice parameter *a* decreased and *c* increased after oxidation. The parameter *b* (twice as large as the basal spacing) increased steeply in the early stage of oxidation, and then very slowly to a constant value. The increase of the basal spacing can be attributed to the decrease of the electrostatic interaction between the interlayer cations and the titanate layers.

In our preliminary study, the interlayer Rb ions of the oxidized manganese titanates could be ion-exchanged with *n*-alkylammonium ions. However, the alkyl chains had mostly a parallel orientation to the titanate layers rather than an inclined arrangement favorable for pillaring. This is due to the reduction of the cation exchange capacity. We are now trying to make space between the layers by changing the orientation of the alkyl chains. The results will be published elsewhere.

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